Intrinsic Viscosity of Methylcellulose Aqueous Solutions

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Introduction

Methylcellulose (MC) is a hydrophobically modified cellulose via partially substituting the hydroxyl groups with methoxide groups. It is a non-toxic, environmentally friendly, and sustainable material. Currently, it is a common thickener and emulsifier widely applied in the food and cosmetics industry[1].

In this study, the intrinsic viscosity of methylcellulose (MC) aqueous solutions was measured using a water-bathed Cannon-Fenske Routine Viscometer and was found to exhibit strong dependence on temperature, molecular weight, and time of annealing. In particular, the intrinsic viscosity increased with lowered temperature and increasing molecular weight. Furthermore, the intrinsic viscosity of a MC aqueous solution were observed to increase with time of annealing at near-theta temperatures, implying the formation of aggregates.

Theory

The intrinsic viscosity characterizes the solute's contribution to the overall viscosity of the solution. The viscosity of dilute polymer solutions η increases with polymer concentration c according to the following approximation, known as the Huggins equation.

$$\eta = \eta_s(1 + [\eta]c + k_H[\eta]^2c^2 + \cdots) \qquad (1)$$

where η_s is the solvent viscosity and $[\eta]$ is the intrinsic viscosity. A modification of Equation (1) gives the following relation

$$\frac{\eta - \eta_s}{\eta_s c} = [\eta] + k_H[\eta]^2c + \cdots \qquad (2)$$

where the constant k_H is the Huggins constant. According to this equation, a linear regression of $(\eta - \eta_s)/\eta_s c$ versus c gives an intercept with the value of $[\eta]$.

Likewise, the following equation known as the Kraemer's equation can be used similarly:

$$\frac{\ln(\eta/\eta_s)}{c} = [\eta] + k_K[\eta]^2c + \cdots \qquad (3)$$

where the constant k_K is the Kraemer's constant, and in theory, for a polymer solution, the difference $k_H - k_K$ should be always 1/2. From the Kraemer's equation, a plot of $\frac{\ln(\eta/\eta_s)}{c}$ versus c gives also an intercept of $[\eta]$, which should agree with the $[\eta]$ determined from Huggins equation.

Experiment

The experimental setup is a Cannon-Fenske Routine Viscometer immersed in a water bath whose temperature is controlled by a heater-chiller system, shown as below.

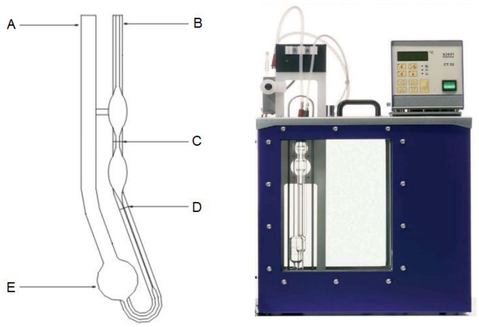

Figure 1 is a sample calculation (Mw = 150k MC solution under 28 ºC, unannealed) procedure used in this experiment in determining an intrinsic viscosity value.

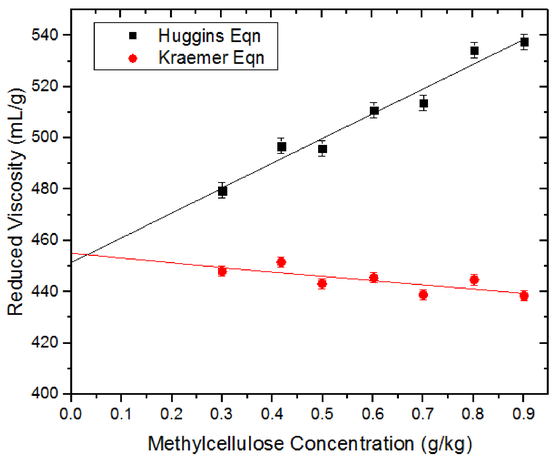

Figure 1. Sample calculation MC-150, under 28 ºC, unannealed

The average of the two intercepts is taken as the intrinsic viscosity. The measured intrinsic viscosity is reported as 453 ± 5 mL/g, which agreed with the literature value of MC-150's intrinsic viscosity provided by Dow Chemical measured by Gel Permeation Chromatography: 473 ± 3 mL/g.

Results and Discussion

The change in intrinsic viscosity of two different molecular weight of MC solutions as a result of temperature variation is shown in Figure 2.

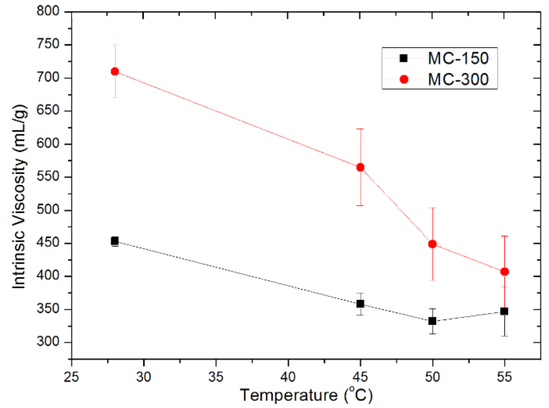

Figure 2. Change of intrinsic viscosity with temperature (un-annealed MC of two different molecular weight)

Generally, MC intrinsic viscosity decreases with an increase of temperature. The decrease in intrinsic viscosity implies that the higher temperature the water, the denser the polymer coil, thus the worse a solvent it is for methylcellulose.

Figure 3 shows the intrinsic viscosity of MC-300 (theta temperature ~ 47 ºC) change with the time of annealing under two near-theta temperatures.

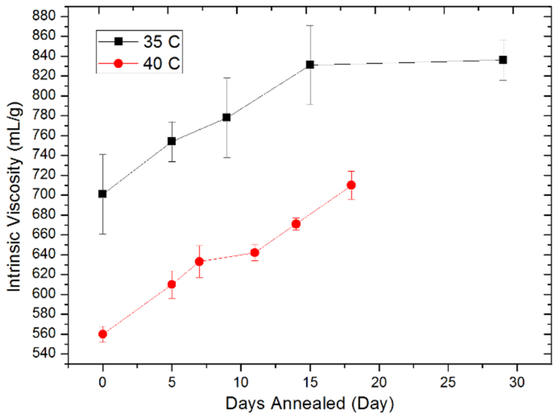

Figure 3. Change of intrinsic viscosity with time of annealing

The trend shown in Figure 3 implies the possibility of MC forming aggregates in the solution under annealing. According to Bodvik et al.[2], the water solubility of MC is attributed primarily to the reduction in number of inter-chain hydrogen bondings due to substitutions of hydroxyl groups by methoxy groups. Yet, for MC with high degree of substitution, the hydrophobicity of methoxy groups would make the polymer insoluble in water.

Water molecules tend to form cage-like structures around small non-polar solutes, it has been suggested that for modified cellulose polymers, water arranges similarly around the hydrophobic groups on the polymer chain. This kind of hydration is enthalpically favorable but entropically unfavorable. Therefore, as the temperature increases, the entropy term becomes more dominant and the free energy of the system is reduced through aggregation[2].

Conclusion

In this study, intrinsic viscosity measurements were used to analyze the conformational change of methylcellulose in aqueous solution. Results showed that intrinsic viscosity tends to be smaller for MC with lower molecular weights and under higher temperature. The annealing under near-theta temperatures led to a growth in intrinsic viscosity with annealing time, the reason was attributed to the formation of aggregates.

Selected References

1. Arvidson, Sara, et al. "Aggregation and network formation in aqueous methylcellulose near the sol-gel transition." APS Meeting Abstracts. Vol. 1. 2012.

2. Bodvik, Rasmus, et al. "Aggregation and network formation of aqueous methylcellulose and hydroxypropylmethylcellulose solutions." Colloids and Surfaces A: Physicochemical and Engineering Aspects 354.1 (2010): 162-171.

Acknowledgement

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